



Short communication

Novel F-doped IrO₂ oxygen evolution electrocatalyst for PEM based water electrolysisKaran Kadakia^{a,1}, Moni Kanchan Datta^{b,e,1}, Prashanth H. Jampani^a, Sung Kyoo Park^b, Prashant N. Kumta^{a,b,c,d,e,*}^a Department of Chemical and Petroleum Engineering, Swanson School of Engineering, University of Pittsburgh, 3700 O'Hara Street, Pittsburgh, PA 15261, USA^b Department of Bioengineering, Swanson School of Engineering, University of Pittsburgh, PA 15261, USA^c Department of Mechanical Engineering and Materials Science, Swanson School of Engineering, University of Pittsburgh, PA 15261, USA^d Department of Oral Biology, School of Dental Medicine, University of Pittsburgh, PA 15217, USA^e Center for Complex Engineered Multifunctional Materials, University of Pittsburgh, PA 15261, USA

HIGHLIGHTS

- Nanostructured IrO₂:F thin films have been wet chemically synthesized.
- Thin film of IrO₂:F (F=20 wt.%) exhibit 19% higher catalytic activity than IrO₂.
- All F doped IrO₂ thin films show higher catalytic activity than pure undoped IrO₂.
- All F doped IrO₂ thin films exhibit comparable durability compared to pure IrO₂.
- Thin films of IrO₂:F are promising anode electrocatalysts for water electrolysis.

ARTICLE INFO

Article history:

Received 20 June 2012

Received in revised form

19 August 2012

Accepted 20 August 2012

Available online 30 August 2012

Keywords:

Water electrolysis

Electrocatalyst

F doped IrO₂

Anode

ABSTRACT

Nanostructured fluorine doped IrO₂ thin film (IrO₂:F) comprising different F contents (5, 10, 15, 20 and 30 wt.%) has been synthesized by thermal decomposition of a homogeneous mixture of IrCl₄ and NH₄F ethanol–DI water solution coated onto pretreated Ti foil. The IrO₂:F thin film on Ti foil has been studied as a promising oxygen evolution anode electrocatalyst for proton exchange membrane (PEM) based water electrolysis. Studies reveal that F-doped IrO₂ with different F content displays remarkably higher electrochemical activity and comparable electrochemical durability in contrast to pure undoped IrO₂ electrocatalyst. Specifically, thin film IrO₂:F with 20 wt.% F shows ~19% higher electrocatalytic activity and comparable durability compared to pure IrO₂ clearly suggesting that F-doped IrO₂ is a better anode and a more efficient electrocatalyst for the oxygen evolution reaction (OER) in PEM based water electrolysis.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen has been considered as an attractive alternative for fossil fuels over the past decade, and holds the potential to be the most lightweight fuel to provide clean, reliable, and affordable energy supply to meet the growing global energy demand [1,2]. One of the major limitation has been the ability to generate hydrogen in a simple, cost effective and efficient manner. One of the promising approaches to produce hydrogen is by electricity

induced splitting of water using alkaline, neutral or proton exchange membrane (PEM) based water electrolysis [1–5]. Electrolysis unfortunately however, at present is not as efficient as the direct chemical path but nevertheless is attractive since it offers virtually no pollution or toxic byproducts particularly, if the electric current is generated using renewable energy (wind, solar, geothermal and hydropower) sources [1–6]. Unfortunately, high capital costs of current electrolyzer technologies are a barrier to attaining the targeted hydrogen production costs comparable to conventional liquid fuels. The high capital costs are caused due to the use of expensive noble metal based electrocatalysts (e.g. IrO₂, RuO₂, Pt), relatively small systems, moderately low efficiencies, customized power electronics, and last but not the least, labor intensive fabrication [1–6]. PEM based water electrolysis which has

* Corresponding author. Department of Chemical and Petroleum Engineering, Swanson School of Engineering, University of Pittsburgh, 3700 O'Hara Street, Pittsburgh, PA 15261, USA. Tel.: +1 4126480223; fax: +1 4126243699.

E-mail address: pkumta@pitt.edu (P.N. Kumta).

¹ Lead authors in the experimental part of this work.

several advantages over the alkaline and neutral water electrolysis employs rutile type expensive noble metal oxides, IrO_2 and RuO_2 as promising oxygen evolution anode electrocatalysts [7–11]. For PEM electrolysis cells a decrease in the precious metal IrO_2 or RuO_2 catalyst loading to ultra-low levels by the development and processing of improved electrochemically active and durable electrocatalysts would significantly decrease the overall capital costs. It has been reported [7–13] that mixed oxides obtained by the addition of cheaper oxides such as SnO_2 , Ta_2O_5 , Nb_2O_5 , TiO_2 to active electrocatalyst IrO_2 and/or RuO_2 (e.g. $\text{IrO}_2\text{--SnO}_2$, $\text{RuO}_2\text{--SnO}_2$, $\text{IrO}_2\text{--Ta}_2\text{O}_5$, $\text{IrO}_2\text{--SnO}_2\text{--Nb}_2\text{O}_5$ etc.) would reduce the cost of the noble metal loading while maintaining the catalytic activity and electronic conductivity similar to the pure noble metal oxide. However, a decrease in the active surface area and electrical conductivity of the mixed oxide in the presence of the inactive diluents has been reported [7–13], and as a result no improvement in the catalytic activity has been noticed with the addition of the cheaper diluents. To the best of our knowledge there have been no technical reports yet published to date documenting the improvements in electrochemical activity of IrO_2 or RuO_2 achieved by alloying with a second element.

In this direction, the present work is carried out to identify a novel dopant/alloying element for the noble metal oxide electrocatalyst (e.g. IrO_2 or RuO_2) in order to improve the catalytic activity compared to pure noble metal oxide electrocatalyst without compromising the corrosion stability of the electrocatalyst. Accordingly, in this article, F-doped IrO_2 thin film, denoted as $\text{IrO}_2\text{:F}$, with 5, 10, 15, 20 and 30 wt.% F has been studied as a promising oxygen evolution anode electrocatalyst exhibiting significant improvement in catalytic activity compared to pure IrO_2 .

2. Experimental details

2.1. Preparation of the electrodes

Iridium tetrachloride [IrCl_4 , 99.5%, Alfa Aesar] and ammonium fluoride [NH_4F , Alfa Aesar] were used as the sources for Ir oxide and F, respectively. Stock solutions corresponding to IrCl_4 of desired compositions were dissolved in absolute ethanol inside an atmosphere controlled glove box (MBraun Unilab Work station) to prevent any undesired side reaction. On the other hand, NH_4F was dissolved in ethanol–deionised (DI) water mixture (5:1 volume ratio). The stock solutions IrCl_4 and NH_4F of desired compositions ($\text{NH}_4\text{F}/\text{IrCl}_4$: 0.04, 0.085, 0.14, 0.19 and 0.33) are then mixed together to synthesize F-doped IrO_2 electrocatalyst with 5, 10, 15, 20 and 30 wt.% F, respectively. The resulting solution was then spin coated on pretreated titanium substrates of $\sim 1\text{ cm}^2$ area (Specialty Coating Systems Inc, Model P6712) with rotating speed of 500 rpm for 10sec. Prior to coating, the Ti substrate was sand blasted and then etched in boiling HCl (30%) for 30 min in order to ensure maximum adhesion of the coating. The HCl treated Ti foil was then washed with purified water generated by the Milli-Q system (18 M Ω cm deionized water, Milli-Q Academic, Millipore) and dried at 130 °C before coating. The thin film precursors deposited on the pretreated titanium substrate were dried at 60 °C for 2 h. Following this treatment, they were thermally treated at 673 K for 4 h in air to decompose the precursors and, as a result $\text{IrO}_2\text{:F}$ film of different compositions are generated on the Ti foils. The loading of the active $\text{IrO}_2\text{:F}$ deposited on the Ti foil is $\sim 0.3\text{ mg cm}^{-2}$ irrespective of the different compositions studied.

2.2. Materials characterization

2.2.1. X-ray diffraction analysis

In order to perform qualitative phase analysis, the $\text{IrO}_2\text{:F}$ thin film electrode of different compositions coated on the Ti foil were

characterized by X-ray diffraction (XRD) using Philips XPERT PRO system employing $\text{CuK}\alpha$ ($\lambda = 0.15406\text{ nm}$) radiation with operating voltage and current at 45 kV and 40 mA, respectively. The XRD peak profile of $\text{IrO}_2\text{:F}$ film of different compositions was analyzed using the Pseudo-Voigt function to determine the Lorentzian and Gaussian contribution of the peaks [14,15]. The integral breadth of the Lorentzian contribution, determined from peak profile analysis using single line approximation method after eliminating the instrumental broadening and lattice strain contribution, is implemented in the Scherrer formula to calculate the effective crystallite size of the $\text{IrO}_2\text{:F}$ electrode of different compositions [14,15]. The lattice parameter and molar volume of $\text{IrO}_2\text{:F}$ of different compositions has been calculated using the least square refinement techniques.

2.2.2. Microstructure analysis

To investigate the microstructure of the thin film electrodes, scanning electron microscopy (SEM) was conducted. Quantitative elemental analysis and distribution of elements (X-ray mapping) was investigated using the energy dispersive X-ray spectroscopy (EDX) analyzer integrated into the SEM machine. Philips XL-30FEG equipped with an EDX detector system comprised of an ultrathin beryllium window and Si(Li) detector operating at 20 kV was employed for the secondary electron (SE) image, elemental and X-ray mapping analyses.

2.2.3. Electrochemical tests

The electrochemical activity of pure IrO_2 and $\text{IrO}_2\text{:F}$ of different compositions, used as an oxygen evolution reaction (OER) anode electrocatalyst for PEM based water electrolysis, was conducted in an electrochemical workstation (VersaSTAT 3, Princeton Applied Research) using a three electrode cell configuration. A solution containing 1 N sulfuric acid (H_2SO_4) was used as the electrolyte while also serving as the source of the fuel. The H_2SO_4 solution is kept at a constant temperature of 40 °C using a Fisher Scientific 910 Isotemp Refrigerator Circulator. Thin films of IrO_2 and $\text{IrO}_2\text{:F}$ of different F content coated on Ti foil were used as the working electrode with an exposed surface area $\sim 1\text{ cm}^2$ and a total loading of $\sim 0.3\text{ mg cm}^{-2}$ for each system. The polarization curve was recorded at a scanning rate of $\sim 1\text{ mV s}^{-1}$ using platinum as the counter electrode and $\text{Hg}/\text{Hg}_2\text{SO}_4$ as the reference electrode that has a potential of +0.65 V with respect to the Normal hydrogen electrode (NHE). In order to study the accelerated life stability of the $\text{IrO}_2\text{:F}$ anode electrode for PEM based water electrolysis, chronoamperometry (CA) (current vs. time) of selected samples has been performed for 24 h using 1 N H_2SO_4 as the electrolyte employing the same three electrode cell configuration at a constant voltage of $\sim 1.65\text{ V}$ with respect to NHE. Elemental analysis of the electrolyte (H_2SO_4), collected after 24 h of CA testing, was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP 6500 duo Thermo Fisher) in order to determine the amount of iridium leached out in the solution from the electrode and assess the chemical stability and durability of the electrocatalyst.

3. Results

Fig. 1 shows the XRD patterns of the thin film $\text{IrO}_2\text{:F}$ with 10, 20 and 30 wt.% F synthesized by thermal decomposition of homogeneous mixture of IrCl_4 and NH_4F ethanol–DI water solution coated on Ti foil at 673 K for 4 h. The XRD patterns of $\text{IrO}_2\text{:F}$ of different compositions, shown in Fig. 1, indicate a rutile type tetragonal structure similar to pure IrO_2 [10] which suggest the formation of complete solid solution of IrO_2 and F without any undesirable phase formation (e.g. IrF_3). The lattice parameter

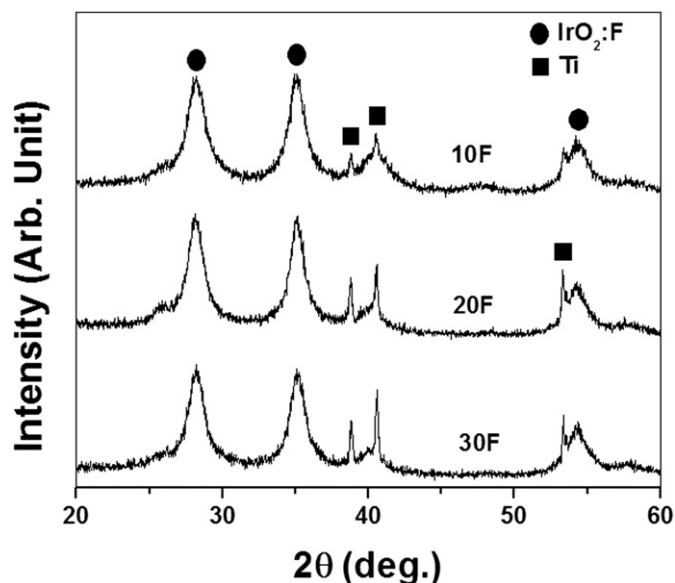


Fig. 1. XRD patterns of thin film $\text{IrO}_2\text{:F}$ with 10, 20 and 30 wt.% F coated on Ti foil.

($a \sim 0.4547$ nm, $c \sim 0.3136$ nm) and molar volume of $\text{IrO}_2\text{:F}$ ($\sim 19.53 \pm 0.04$ cm³ mol⁻¹) of different compositions, calculated using least square refinement techniques, is comparable with pure IrO_2 ($\sim 19.64 \pm 0.04$ cm³ mol⁻¹) [10] which suggest that F⁻ substitution for O²⁻ has no significant effect on the molar volume of $\text{IrO}_2\text{:F}$. This may be largely due to the fact that the ionic radius of O²⁻ (125 pm) is comparable with F⁻ (120 pm). The effective crystallite size of $\text{IrO}_2\text{:F}$, calculated using the Scherrer formula from the integral breadth of the Lorentzian contribution determined from peak profile analysis using single line approximation method after eliminating the instrumental broadening and lattice strain contribution [14,15], is in the range of ~ 4 – 6 nm irrespective of compositions indicating the nanocrystalline nature of the catalyst. The presence of elemental Ir and O in the $\text{IrO}_2\text{:F}$ film of different compositions has also been confirmed using energy dispersive X-ray spectroscopy analysis (EDX) attached to the SEM. However, the presence of F could not be detected in the EDX analysis. Suitable spectroscopic techniques, such as wavelength dispersive X-ray fluorescence and Rutherford backscattering, needs to be used for accurate determination of F in the F-doped IrO_2 [16]. It must also be mentioned here however that the real F content in $\text{IrO}_2\text{:F}$ thin film will be different than the starting composition due to the expected loss of F (high volatility) during thermal decomposition of the starting precursors at 673 K [16]. The SEM image along with EDX of the $\text{IrO}_2\text{:F}$ film with 10 wt.% F, shown in Fig. 2a and b, respectively, indicates the presence of Ir and O, and the characteristic sintered “mud crack” type morphology of $\text{IrO}_2\text{:F}$ film coated on the Ti foil typically seen for chemically derived thin films.

The electrochemical activity of the nanocrystalline thin film of $\text{IrO}_2\text{:F}$ of different F compositions has been studied as a suitable oxygen evolution anode electrocatalyst for PEM based water electrolysis. The polarization curve of pure IrO_2 and $\text{IrO}_2\text{:F}$ film of different F compositions, conducted in the presence of 1 N H_2SO_4 solution at 40 °C with a scan rate of 1 mV s⁻¹, shown in Fig. 3, clearly indicates that the oxygen evolution reaction (water splitting) occurs at a potential of ~ 1.4 V vs. NHE irrespective of the varying F compositions. The polarization curve of $\text{IrO}_2\text{:F}$ of different F compositions, plotted in Fig. 3, shows that the electrochemical activity of $\text{IrO}_2\text{:F}$ increases with increasing F content up to ~ 20 wt.% F. It must be mentioned here that the present results do not exclude the ohmic loss (iR loss) in the polarization curve which

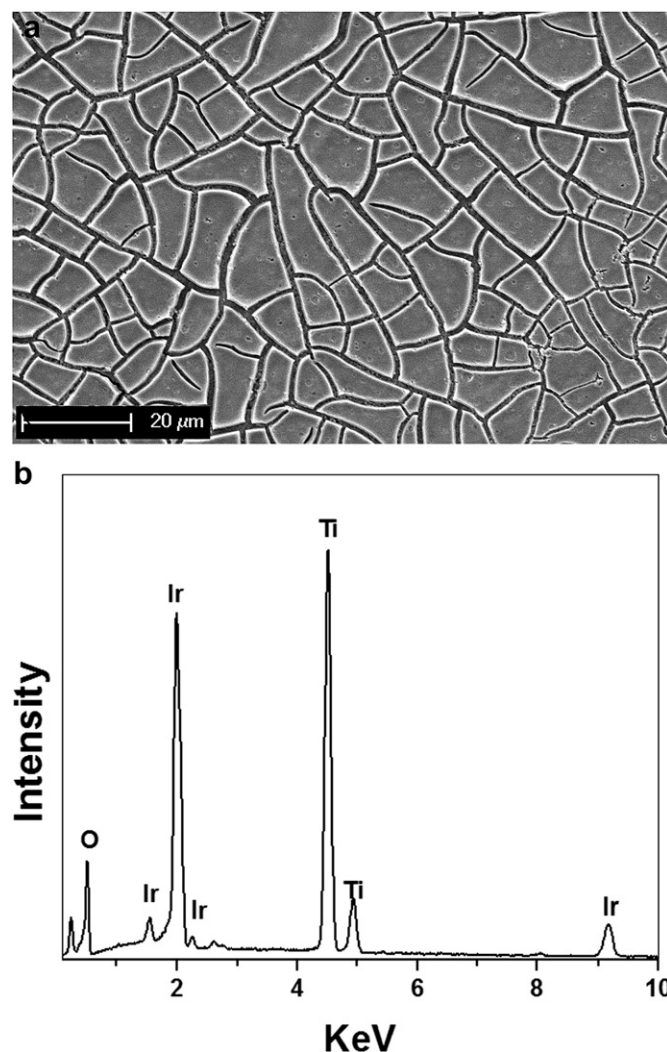


Fig. 2. The SEM micrograph (a) along with EDX (b) of $\text{IrO}_2\text{:F}$ film with 10 wt.% F.

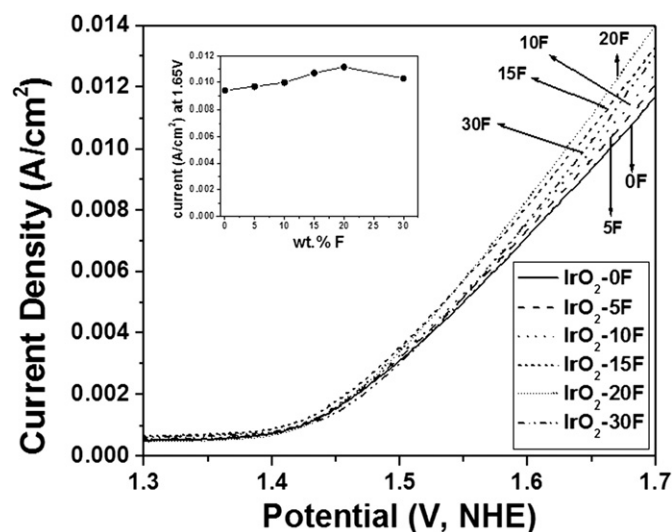


Fig. 3. The polarization curve of pure IrO_2 and fluorine doped $\text{IrO}_2\text{:F}$ film of different F compositions conducted in the presence of 1 N H_2SO_4 solution at 40 °C with a scan rate of 1 mV s⁻¹. The inset shows the variation of current density at ~ 1.65 V (vs. NHE) with F content of the doped $\text{IrO}_2\text{:F}$ anode electrocatalyst.

is known to arise mainly due to the solution resistance. In the present study, the solution resistance irrespective of the electrode composition has been determined from electrochemical impedance spectroscopy to be approximately, $\sim 16 \Omega$. The current density at ~ 1.65 V of $\text{IrO}_2\text{:F}$ for different F compositions with a total loading $\sim 0.3 \text{ mg cm}^{-2}$, plotted and shown in the inset in Fig. 3, indicates that the current density of $\text{IrO}_2\text{:F}$ increases up to 20 wt.% F beyond which there is a decrease in the current density suggesting a reduction in the electrochemical activity. The $\text{IrO}_2\text{:F}$ with 20 wt.% F shows a current density of $\sim 0.0116 \pm 0.0001 \text{ A cm}^{-2}$ which is $\sim 19\%$ higher to that of pure IrO_2 ($\sim 0.0094 \text{ A cm}^{-2}$) at ~ 1.65 V. On the other hand, it has been noticed that the current density decreases with increase in F content above 20 wt.% F. The possible reasons contributing to the improvement in electrochemical activity of F-doped IrO_2 compared to pure IrO_2 and the optimum value of fluorine determined to be 20 wt.% F can be understood from a series of *ab-initio* calculations results of which will be published very shortly by the present authors (ref. [17]). These calculations involve considerations of the chemical species, the basic intermediate chemical reaction steps, and the rate determining step involved in the electrolytic water splitting process. A summary of the detailed analysis of the electronic structure of the F-doped IrO_2 shows that the p,d-hybridization between Ir5d- and F2p-states is the primary reason contributing to a decrease in energy of the rate determining step of the electrolysis reactions, hence resulting in a substantial improvement in the electrochemical activity showing a maximum at 20 wt.% F. The above results clearly suggest that $\text{IrO}_2\text{:F}$ of different F content exhibits higher electrochemical activity compared to pure IrO_2 , and is a promising candidate oxygen evolution anode electrocatalyst for PEM based water electrolysis.

In order to study the corrosion and structural stability of the anode electrocatalyst $\text{IrO}_2\text{:F}$ in 1 N H_2SO_4 , chronoamperometry (CA) test is conducted for 24 h at 40°C at a constant voltage of 1.65 V. The CA curves, obtained at a constant voltage of ~ 1.65 V, of $\text{IrO}_2\text{:F}$ with 5, 10 and 20 wt.% F along with pure IrO_2 , are shown in Fig. 4. The $\text{IrO}_2\text{:F}$ electrodes categorically show higher initial current with increase in F content due to their higher oxygen evolution activity as demonstrated in the polarization curves (see Fig. 3). The CA curve shows a marked decay of current (10% of the initial value) for all electrodes in the initial 1 h which may arise either due to significant dissolution of the irregular coatings

located at the edge of the mud cracks [18] or diffusion controlled reaction. A steady decay of current (13% after 24 h in comparison with the 1 h value) has been noticed after 1 h of initial period for $\text{IrO}_2\text{:F}$ and pure IrO_2 which suggests that $\text{IrO}_2\text{:F}$ (up to 20 wt.% F) has similar structural stability compared to pure IrO_2 . However, the ICP results, conducted in the H_2SO_4 electrolyte solution collected after 24 h of CA measurement, show no presence of Ir up to 20 wt.% F doping which suggest the steady decay of current of $\text{IrO}_2\text{:F}$ during CA measurement (Fig. 4) may arise due to loss of fuel rather than the dissolution of the IrO_2 electrocatalyst. In the present experimental condition, it has been noticed that ~ 9 ml fuel has been lost after 24 h of CA measurement for 20 wt.% F doped IrO_2 due to the high OER activity. The present study therefore successfully identifies $\text{IrO}_2\text{:F}$ as a promising anode electrocatalyst with the ability to significantly improve the electrocatalytic performance and electrochemical stability. The $\text{IrO}_2\text{:F}$ anode electrocatalysts can therefore be expected to exhibit significant reduction in capital cost of PEM based water electrolyzers due to the significant improvement in the electrochemical activity and stability as outlined by the present studies.

4. Conclusion

Nanostructured F-doped IrO_2 of different F content (5–30 wt.% F) coated as a thin film on pretreated Ti foil has been studied as a promising oxygen evolution anode electrocatalyst for PEM based water electrolysis. A homogeneous mixture of IrCl_3 and NH_4F ethanol–DI water solution in a wide range of compositions was coated on pretreated Ti foil and heat treated at 673 K for 4 h to synthesize F-doped IrO_2 electrocatalyst with 5, 10, 15, 20 and 30 wt.% F. The molar volume of $\text{IrO}_2\text{:F}$ of different compositions, calculated from least square refinement techniques, is comparable with pure IrO_2 which suggest that F^- doping in place of O^{2-} has no significant effect on the molar volume of $\text{IrO}_2\text{:F}$. The crystallite size of $\text{IrO}_2\text{:F}$, calculated from least square refinement techniques, is in the range of ~ 4 – 6 nm irrespective of the F content. The electrochemical performance of $\text{IrO}_2\text{:F}$ with different F content as a promising oxygen evolution electrocatalyst has been carried out in the presence of 1 N H_2SO_4 as a fuel at 40°C . The electrochemical activity measured as a current at 1.65 V (vs. NHE), of $\text{IrO}_2\text{:F}$ shows that the catalytic activity increases with increase in F content up to 20 wt.% F. The F-doped IrO_2 with 20 wt.% F shows $\sim 19\%$ higher catalytic activity and comparable durability in contrast to pure IrO_2 . The excellent electrochemical activity exhibited by F-doped IrO_2 along with the proven long term structural stability makes it an ideal candidate as anode electrocatalysts for oxygen evolution in PEM based water electrolysis.

Acknowledgements

Research supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-SC0001531. Authors also acknowledge Pittsburgh Supercomputing Center for allocation of computational resources. PNK acknowledges the Edward R. Weidlein Chair Professorship funds and the Center for Complex Engineered Multifunctional Materials (CEMM) for procuring the electrochemical equipment used in this research work.

References

- [1] M.F. Hordoski, Hydrogen and Fuel Cells-Advances in Transportation and Power, Fairmont Press, 2009.
- [2] Hydrogen Production Technical Team, Hydrogen Production Road Map: Technology Pathways to the Future, FreedomCAR & Fuel Partnership, 2009.
- [3] K. Zeng, D. Zhang, Prog. Energy Combust. Sci. 36 (2010) 307.

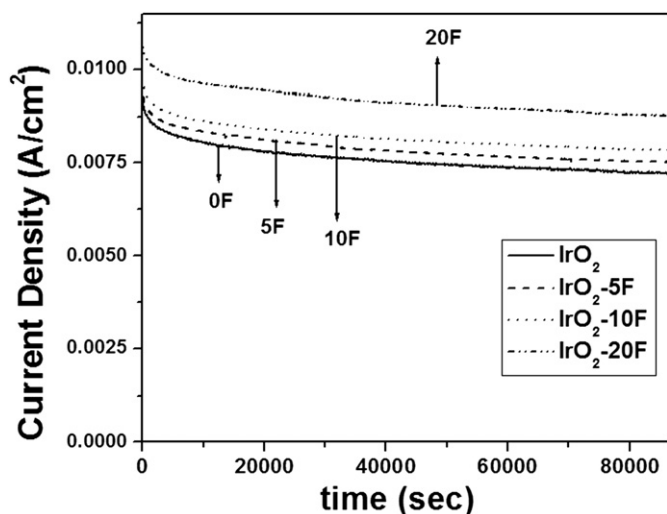


Fig. 4. Variation of current vs. time in the accelerated life test of pure IrO_2 and $\text{IrO}_2\text{:F}$ with 5, 10, 20 wt.% F performed in a 1 N H_2SO_4 solution under ~ 1.65 V at 40°C .

- [4] M.W. Kanan, D.G. Nocera, *Science* 321 (2008) 1072.
- [5] P. Millet, N. Mbemba, S.A. Grigoriev, F.N. Fateev, A. Aukauloo, C. Etievant, *Int. J. Hydrogen Energy* 36 (2011) 4134.
- [6] R.E. Clarke, S. Giddey, S.P.S. Badwal, *Int. J. Hydrogen Energy* 35 (2010) 928.
- [7] E. Mayousse, F. Maillard, F. Fouda-Onana, O. Sicardy, N. Guillet, *Int. J. Hydrogen Energy* 36 (2011) 10474.
- [8] A. Marshall, B. Børresen, G. Hagen, M. Tsyppkin, R. Tunold, *Electrochim. Acta* 51 (2006) 3161.
- [9] C.P. De Pauli, S. Trasatti, *J. Electroanalytical Chem.* 396 (1995) 161.
- [10] K. Kadakia, M.K. Datta, O.I. Velikokhatnyi, P. Jampani, S.K. Park, P. Saha, J.A. Poston, A. Manivannan, P.N. Kumta, *Int. J. Hydrogen Energy* 37 (2012) 3001.
- [11] X. Wu, K. Scott, *Int. J. Hydrogen Energy* 36 (2011) 5806.
- [12] M. Morimitsu, R. Otagawa, M. Matsunaga, *Electro. Acta* 46 (2000) 401.
- [13] S. Ardizzzone, C.L. Bianchi, G. Cappelletti, M. Ionita, A. Minguzzi, S. Rondinini, A. Vertova, *J. Electroanalytical Chem.* 589 (2006) 160.
- [14] T.H. de Keijser, J.I. Langford, E.I. Mittemeijer, A.B.P. Vogels, *J. Appl. Crystallogr.* 15 (1982) 308–314.
- [15] M.K. Datta, "Synthesis and characterization of Fe–Ni–Si system synthesized by mechanical alloying" Ph.D. Thesis, Indian Institute of Technology, Kharagpur, India, 2002.
- [16] A.A. Shaltout, H.H. Afify, S.A. Ali, *J. Elec. Spect. Relat. Phenom.* 185 (2012) 140.
- [17] O. I. Velikokhatnyi, K. Kadakia, M. K. Datta, P. N. Kumta, *J. Phys. Chem. C*, submitted for publication.
- [18] J.M. Hu, H.M. Meng, J.Q. Zhang, C.N. Cao, *Corros. Sci.* 44 (2002) 1655.